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Aluminum Reclamation by Acidic Extraction of Aluminum-Anodizing Sludges

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16. ABSTRACT

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Aluminum reclamation by acidic extraction of aluminum-anodizing sludges

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ABSTRACT: Extraction of aluminum-anodizing sludges with sulfuric acid was examined to determine the potential for production of commercial-strength solutions of aluminum sulfate, that is liquid alum. This research establishes kinetic and stoichiometric relationships and evaluates product quality. Detailed material-balance data were collected to monitor the progress and extent of extractions. The production of a commercial-strength liquid alum was feasible. Issues relative to product quality indicate that segregation of certain metal containing wastes may be required for selected aluminum-finishing wastes. *J. Water Pollut. Control Fed.*, **60**, 369 (1988).

KEYWORDS: Industrial waste, metal finishing, (metal recovery), aluminum anodizing, sludge reclamation.

Conventional aluminum-finishing wastewaters contain aluminum as a primary constituent and are typically treated by neutralization, polymer conditioning, flocculation, and sedimentation with sludge dewatering before land disposal. Clarified effluents are recycled as rinsewater or discharged into a municipal sewer or surface waters. Sludges produced contain aluminum in the form of aluminum-hydroxide precipitates and other precipitated or complexed metals.[1]

From industrial waste surveys conducted at two aluminum-anodizing plants, the mass of wet dewatered sludge was equal to 53 and 86% of the mass of finished aluminum products while, on a dry-weight basis, the proportions were 8.5 and 14%.[1,2] These values indicate the magnitude of the sludge disposal problem typically faced by aluminum-anodizing plants. With the application of increasingly stringent regulations on the disposal of industrial sludges and the long-term liability associated with land disposal, sludge disposal is an area of major economic and environmental concern for the industry. Although these sludges are not categorically listed as "hazardous," regulations on all industrial sludges are affected by those imposed on hazardous sludges, if through no other mechanism than the escalation of sludge hauling and disposal costs. Therefore, pursuit of reclamation options for these gelatinous aluminum-anodizing sludges is to be encouraged.

Previous research[2,3] established process feasibility for aluminum-anodizing sludges; however, data focused on process optimization. Product quality data are still needed. Considerable data are available on the extraction of aluminum from water-treatment-plant sludges, that is, "alum" sludges.[2,3] Alum sludges and aluminum-anodizing sludges both contain aluminum hydroxide as a primary constituent, making the aluminum extraction technology for alum sludges generally applicable to aluminum-anodizing sludges.

Commercial-grade liquid alum is produced by extraction of bauxite and other aluminum-rich clays with excess sulfuric acid at elevated temperatures for extended reaction periods. Residual, or inert, solids are removed from acid extracts by polymer conditioning and gravity sedimentation. The clarified alum product is diluted with water used to wash the thickened inert solids. Commercial-grade liquid alum is marketed at concentrations of 3.0 to 8.3% as Al_2O_3 because crystallization temperatures increase rapidly as alum concentrations increase above these values. For example, crystallization temperatures are 42°C, 57°C, and 66°C for alum products at concentrations of 9, 9.5, and 10% as Al_2O_3, respectively, while the crystallization temperatures for liquid alum at concentrations of 8.0 to 8.3% as Al_2O_3 are −15 and −16°C, respectively. Liquid alum may contain iron at levels of 0.4% as Fe_2O_3, while a higher grade product, referred to as "iron-free" alum, typically contains iron at less than 0.005% as Fe_2O_3.[4]

This study examines the acidic extraction of aluminum-anodizing sludges with regard to relative reaction kinetics and stoichiometry, final product quality, and overall process feasibility. Trace metals concentrations were examined to compare sludge-based products with commercially available products. The overall objective was to provide the industry with sufficient data to allow for consideration of implementation of aluminum extraction as an alternative to current sludge disposal practices.

Materials, Methods, and Procedures

Materials. Wastewater samples were obtained from Plant A, an extrusion/anodizing plant producing architectural aluminum extrusions. The aluminum finishing system at Plant A included: alkaline cleaning; caustic-soda etching; acidic desmut; conventional and two-step sulfuric-acid anodizing; and acidic sealing. Continuously-overflowing, recycled-water rinses followed all finishing steps except the acidic seal.

Wastewater treatment at Plant A consisted of three-stage pH neutralization, polymer flocculation, and gravity

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sedimentation. Clarified wastewater is stored for reuse in rinse tanks, or overflows to a municipal sewer system. Sludge treatment consists of vacuum filtration of underflow sludge suspensions followed by contract hauling and land disposal of dewatered sludges. A schematic diagram of the wastewater treatment facility is presented in Figure 1. Spent finishing acids are segregated and used in pH neutralization. The caustic-soda etching system at this plant is an extended-life, no-dump system with no routine discharge of spent etch. Spent or virgin caustic-soda solutions are used to adjust pH in the neutralization system but the characteristically alkaline, influent wastewater results in a limited demand for caustic soda in neutralization. This treatment system is very common to the industry and is referred to as a conventional-neutralization treatment system.

Wastewaters were obtained from Plant A by collecting clarifier underflow. Dewatered sludge cakes were produced in a 250-mm, pilot-scale, filter press at the plant site. The pressure filter was operated using house-air pressure at 6–7 bar (87–100 psi) for approximately 1.5 hours and each filter run produced two wet sludge cakes (mass ≅ 1 kg/cake), which were stored in sealed polyethylene bags for immediate transport to the laboratory. Upon arrival, sludge cakes were analyzed for dry (103°C) and fixed (550°C) solids[5] and stored at 2–5°C before acidic extraction.

Experimental data presented herein were developed by sulfuric-acid extractions of two sets of similar sludge cakes produced on two separate days at Plant A. Both sets of sludge cakes were produced within 2 weeks of each other during normal operations at Plant A. The acid used during the experimental extractions was concentrated reagent-grade sulfuric acid.

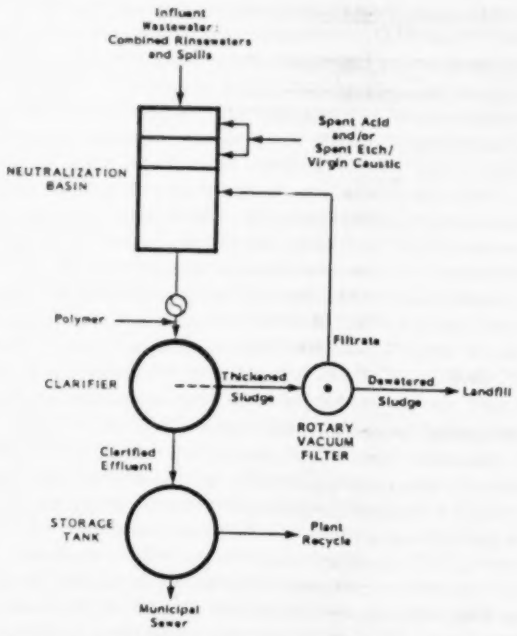

Figure 1—Schematic diagram of wastewater treatment system at Plant A.

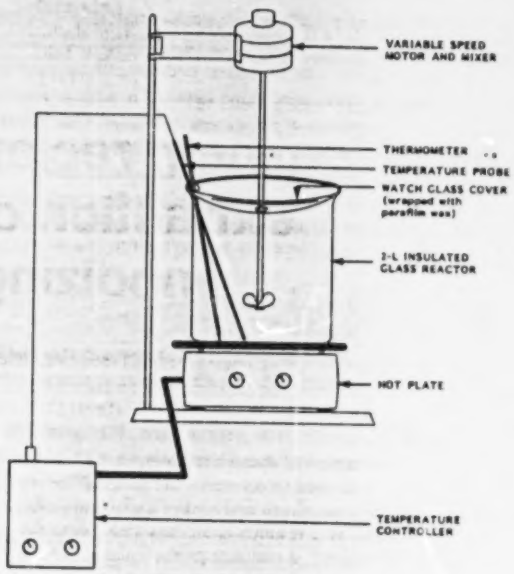

Figure 2—Schematic diagram of experimental extraction reactor.

Experimental reactor. Sulfuric acid extractions of sludge cakes were conducted in a laboratory-scale batch reactor, shown schematically in Figure 2. The reactor consisted of an insulated 2-L glass beaker, watch glass cover, polyethylene stirring paddle attached to a variable speed motor, thermometer, and temperature-controlled hot plate. During extractions, the watch glass cover was wrapped with parafilm wax to minimize evaporation. Extractions were conducted at temperatures between 50 and 90°C under vigorous mixing conditions following manual addition of sulfuric acid. Samples were withdrawn intermittently to monitor reaction progress by lifting the watch glass cover and manually mixing the reactor contents to ensure representative sampling. Manual mixing was necessary because the stirring paddle was removed to gain access to the reactor. Extractions were conducted for 6- and 24-hour reaction times.

Procedures. Extractions were conducted by adding sulfuric acid to aluminum-anodizing sludge cakes. To extract all available aluminum and produce a product that was not excessively acidic, a procedure was developed to establish the sulfuric acid quantity required to complete an extraction. The stoichiometric quantity of sulfuric acid can be calculated according to the following chemical equation:

$$2Al(OH)_3 + xH_2O + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + (6 + x)H_2O, \quad (1)$$

provided it is assumed that cake solids were represented by $Al(OH)_3$ and the quantity of moisture associated with cake solids can be represented by x.

From Equation 1, the acid requirement is 1.89 g H_2SO_4/g $Al(OH)_3$. From previous research it was shown that the aluminum content of the fixed solids in conventional neutralization sludge cakes varied from 32.4 to 39.7%, and was in general agreement with a 34.6% value for the aluminum content of $Al(OH)_3$. Therefore, using the fixed solids content of the dewatered sludge cakes, the acid requirements for extractions were calculated using the value of 1.89 g H_2SO_4/g fixed solids. This approximate dose was based on the assumption that fixed solids were composed of $Al(OH)_3$. Furthermore, based on measured concentrations of dry and fixed solids, as well as the added dosage of sulfuric acid, the final product alum concentration could be estimated. Commercial-grade liquid alum strengths are typically presented in terms of Al_2O_3. As an example, a 1000 g (wet) aliquot of a sludge cake with a dry solids content of 21.3% and a fixed solids content of 16.8% contains 832 g of moisture and requires 318 g of H_2SO_4. Conserving all added mass, the final product would be 28% as $Al_2(SO_4)_3$ or 8.3% as Al_2O_3. In these calculations, it was assumed that the additional loss in mass following exposure to 550°C was indicative of the bound moisture loss associated with highly gelatinous aluminum-hydroxide precipitates.

An alternative to using fixed solids as a measure of $Al(OH)_3$ content consisted of analytically determining aluminum concentrations in dewatered sludge cakes. From Equation 1, the stoichiometric acid requirement would be 5.44 g/g Al. The procedure based on determination of acid requirements using fixed solids was used in all sludge cake A-1 extractions. The latter stoichiometric requirement, based on direct aluminum measurements, was used after these extractions to evaluate the actual acid dose. For all extractions of cake A-2, the acid dose was based on the stoichiometric requirement calculated using direct measurement of sludge aluminum content.

To investigate the acidic extraction reaction regarding relative reaction kinetics and stoichiometry, final product quality, and overall process feasibility, the following experimental strategy was developed. Sulfuric-acid extractions were conducted in the experimental reactor at various control temperatures and levels of sulfuric acid addition. The kinetic progress of the reaction was monitored by sample withdrawals at various intervals throughout an experimental run. A material balance on total mass, as well as aluminum, was conducted on each extraction to account for the fate of various constituents (for example, sludge solids, residual aluminum, soluble aluminum, and acid) throughout an extraction. For example, aluminum mass is conserved throughout an extraction and at any point aluminum may exist in the solid phase (that is, contained in unextracted sludge-cake solids) and the liquid phase (for example, as soluble aluminum sulfate). Therefore, a mass balance on aluminum contributed from both phases provides an accurate description of the conversion of solid-phase aluminum to soluble aluminum during an extraction. A material balance across the system also provides a check on analytical procedures and techniques.

To initiate an extraction, a wet sludge cake was removed from storage at 2–5°C, weighed (to the nearest 0.5 g), and placed into the reactor. Based on a fixed solids or an elemental aluminum analysis, the quantity of required sulfuric acid was calculated according to Equation 1. Acid was slowly added over several minutes to the reactor, because of the vigorous nature of the acid-sludge reaction. Because an excessive acid addition rate resulted in the production of foam that would overflow the reactor, avoiding excessive foam production regulated the acid addition rate. Following acid addition, the reactor was covered and mixing was initiated. Initial temperatures because of the heat of hydration from sulfuric acid addition reached as high as 91°C. Following this elevation of temperature, the reactor was then allowed to cool to and regulated at the desired control temperature (for example, 50° to 90°C). The reactor cover was wrapped with parafilm wax to minimize evaporation and heat losses during an extraction.

Samples were withdrawn at various intervals throughout the reaction for analysis. The initial sample was withdrawn only after the solids had been sufficiently suspended in the acid and a representative sample of the suspension could be acquired. This was typically achieved within 0.5 hour of initiation of an extraction. The sampling procedure consisted of terminating mixing and disconnecting the stirring paddle shaft; removing the parafilm wax, and manually mixing the reactor contents while pouring a sample aliquot of approximately 100 mL into pre-weighed sample containers. The reactor was re-assembled and mixing and heat addition were continued within approximately two to three minutes. Sample preparation consisted of weighing the tared sample container with contents followed by filtration of approximately 15 mL through a 0.45-μm membrane filter.

Analytical methods. Sample filtrates were analyzed for Al_2O_3 concentration, free Al_2O_3/free acid content, and iron content according to conventional analytical procedures.[4] The determination of Al_2O_3 concentration is based on aluminum complexation with a slight excess of EDTA and back titration of the excess EDTA with a standard zinc sulfate solution.[4] Determination of free Al_2O_3 or free acid is accomplished by adding a known amount of acid, adding potassium fluoride to prevent aluminum sulfate hydrolysis, and back titrating the excess acid.[4] Iron content was measured following iron reduction to the ferrous form and titration with potassium dichromate.[4]

Alum filtrates were analyzed for aluminum by atomic absorption spectroscopy.[5] Samples were analyzed for pH using a 2% dilution. Suspended solids (SS) concentrations were measured.[5] Specific gravity was determined by weighing 25 mL of sample in a tared 25-mL volumetric flask. Note that sample volumes for specific gravity and SS procedures were measured at the same temperature to accurately calculate the residual solids mass in a given sample. Acidity was qualitatively determined according to a congo red test provided by alum producers.[6] This procedure is used to determine the presence of free alum or free acid in an alum sample by examining color changes that occur as an alum digest approaches, attains, and passes through neutrality, and then begins to dissolve free Al_2O_3.

Additionally, a final sample of an extraction and commercial alum samples were analyzed for trace metals using an inductively coupled plasma source (ICP) and atomic

absorption spectroscopy.[5] The samples were analyzed for cadmium, chromium, silver, lead, zinc, nickel, and tin. All experimental-reactor system components, as well as sample containers and analytical equipment, were cleaned in 1:1 nitric acid solutions and stored in deionized water before each extraction to protect against sample contamination.

Experimental Results

Sludge properties. Characteristics of the sample sludge cakes are presented in Table 1. The dry solids contents of both sludge cakes were slightly higher than those typically produced by vacuum filtration of the clarifier underflow suspensions at Plant A. The dry solids contents of 18.1 and 17.4% for sludge cakes A-1 and A-2, respectively, were less than the estimated values, that is, 21 to 24% dry solids, required to produce a liquid alum of 8.0% as Al_2O_3.[2]

Aluminum contents of 35.6 and 39.2% for sludges A-1 and A-2, respectively, were typical of conventional neutralization sludges and consistent with the theoretical value of 34.6% for $Al(OH)_3$.[1] Therefore, it was initially assumed that fixed solids could be used as an indirect measure of aluminum hydroxide solids. Sludge aluminum contents were also higher than the 19.5% value reported for bauxite.[3] Therefore, on a dry weight basis, the aluminum-anodizing sludges contained more aluminum than bauxite, which is used for the production of commercial-grade liquid alum, and seemed to have potential for the production of liquid alum.

Acidic extractions. Sulfuric acid extractions were conducted on sludge cakes A-1 and A-2 under various conditions. The overall objective was to extract all aluminum from the sludge cakes as soluble aluminum sulfate and produce a final product with a concentration of at least 8.0% as Al_2O_3. However, according to the fixed solids contents presented in Table 1, both sludges contained less than the minimum amount of aluminum to produce an alum with a concentration of 8% as Al_2O_3. Therefore, concentrations less than 8.0% as Al_2O_3 would be expected unless significant evaporation resulted in a more concentrated final product.

The initial experimental conditions for three extractions conducted using sludge cake A-1 are presented in Table 2. Sulfuric acid requirements were calculated according to Equation 1 using fixed solids as a measure of aluminum hydroxide. From Table 1 it is noted that the measured aluminum content for sludge cake A-1 is greater than the theoretical value for aluminum hydroxide. Therefore, calculated acid requirements using fixed solids as a measure of aluminum hydroxide were less than the actual acid dosages required according to the aluminum contained in the sludge. As indicated in Table 2, acid dosages were between 89.2 to 97.2% of the stoichiometric amount based on available aluminum. All sludge samples were analyzed for dry and fixed solids before sludge extractions and these results are included in Table 2. The data for Run 1-2 indicated that the sludge cake had apparently accumulated moisture during storage and preparation for the extraction. Therefore, the theoretical estimated alum concentration decreased to 5.9% as Al_2O_3. Estimated alum concentrations for Runs 1-1 and 1-3 were 7.3 and 7.1% as Al_2O_3, respectively, with the minor differences being attributed to variations in the level of acid addition.

The variations in temperature of the extractions of sludge cake A-1 are presented in Figure 3. Although not

Table 1—Characteristics of dewatered sludge cakes from Plant A.

Parameter	Sludge cake A-1	Sludge cake A-2
Dry (103°C) solids, content, g dry solids/100 g wet cake	18.1	17.4
Fixed (550°C) solids content, g fixed solids/100 g wet cake	13.3	13.9
Aluminum content, g Al/100 g fixed solids	35.6	39.2

Table 2—Initial experimental conditions for extractions of sludge cake A-1.

Parameter	Run 1-1	Run 1-2	Run 1-3
Sludge addition			
Total mass, g	709.5	541.0	744.5
Fixed solids, g	94.4	56.8	98.7
Moisture, g	615.1	484.2	645.8
Sulfuric acid			
Sulfuric acid addition, g[a]	163.5	107.1	186.1
Percent of stoichiometric acid dosage, percent[b]	89.2	97.2	97.2
Control temperature, °C	90	70	50
Estimated product concentration, percent as Al_2O_3[c]	7.3	5.9	7.1

[a] Sulfuric acid addition calculated according to Equation 1 using fixed solids as a measure of aluminum hydroxide.
[b] Percentage based on acid required according to Equation 1 using actual measured aluminum content.
[c] Estimated alum concentration calculated according to Equation 1 using actual measured aluminum content.

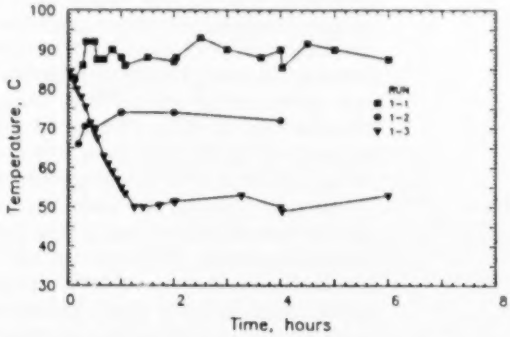

Figure 3—Temperature of reactor contents during acidic extraction of sludge cake A-1.

included in the figure, the sludge cakes were near ambient temperature before adding acid. Upon acid addition, the temperature of Runs 1-1 and 1-3 increased to 83 to 85°C, while Run 1-2 was at 66°C. Runs 1-1 and 1-2 remained near the initial value throughout the run, while Run 1-3 was allowed to cool to the desired control temperature of 50°C over a 1.1-hour period before the temperature-control system was activated. Because of the highly exothermic reaction following the addition of acid and the dramatic elevation of reactor temperatures, the temperature control system was activated 0.13 hours, 0.2 hours, and 1.1 hours after the addition of acid, respectively, for Runs 1-1, 1-2, and 1-3. After initiation of temperature control procedures, the average reaction temperatures (and associated standard deviations) were 89°C (2.7°C), 71°C (3°C), and 51°C (1.6°C) for Runs 1-1, 1-2, and 1-3. These actual temperatures were well within one standard deviation of the desired control temperature.

Filtrate aluminum concentrations for the three extractions using sludge cake A-1 are presented in Figure 4. Other parameters relative to product quality measured during each extraction did not vary significantly with time, and are presented later. From Figure 4, it is apparent that most of the sludge solids were extracted during the initial 0.5-hour period. Beyond this period, additional increases in aluminum concentration were attributed to solubilization of residual solids as well as evaporation losses. Runs 1-1 and 1-3 reached estimated product concentration values in the initial 0.5 hour, indicating that the extractions were near completion. Additionally, SS concentrations had decreased by 93 and 94.8%, respectively, for Runs 1-1 and 1-3 during the initial period.

Although data for the extended time period are not shown in Figure 4, Run 1-2 was conducted for approximately 24 hours with aluminum concentrations of 7.3 and 7.5% as Al_2O_3 being achieved at 19.4 and 24.6 hours, respectively. The increase in Al_2O_3 concentrations during the 24-hour period was associated with evaporational losses. During the initial 0.5 hour of Run 1-2, an aluminum concentration of 6.7% as Al_2O_3, which was higher than the estimated product concentration of 5.9% as Al_2O_3, was achieved. This difference could be attributed to significant losses in sample mass because of evaporation as well as analytical errors associated with dry and fixed solids measurements.

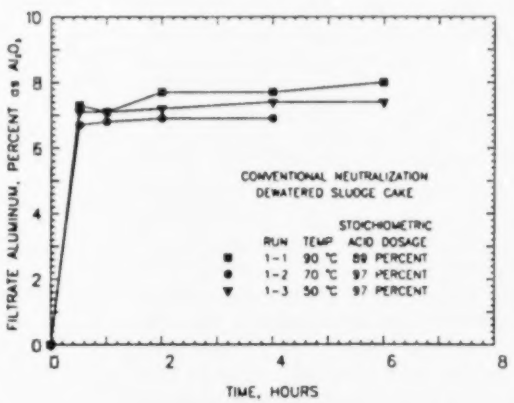

Figure 4—Filtrate aluminum concentrations during acidic extraction of sludge cake A-1.

Table 3—Initial experimental conditions for extractions of sludge cake A-2.

Parameter	Run 2-1	Run 2-2
Sludge addition		
Total mass, g	611.5	641.5
Fixed solids, g	84.9	89.4
Moisture, g	526.6	552.1
Sulfuric acid		
Sulfuric acid addition, g[a]	181.4	191.0
Percent of stoichiometric acid dosage, percent[b]	100.0	100.0
Control temperature, °C	90	50
Estimated product concentration, percent as Al_2O_3[c]	7.9	8.0

[a] Sulfuric acid addition calculated according to Equation 1 using fixed solids as a measure of aluminum hydroxide.
[b] Percentage based on acid required according to Equation 1 using actual measured aluminum content.
[c] Estimated alum concentration calculated according to Equation 1 using actual measured aluminum content.

Initial experimental conditions for two extractions conducted using sludge cake A-2 are presented in Table 3. Sulfuric acid requirements were calculated according to Equation 1 using the measured aluminum content for sludge A-2 (presented in Table 1), and were, therefore, equal to 100% of the stoichiometric requirement. Sludge cake A-2 had a fixed solids content of 13.9% compared to the 13.3% value for sludge cake A-1. Furthermore, sludge cake A-2 had an aluminum content of 39.2% (based on fixed solids) compared to the respective value of 35.6% for cake A-1. With the higher fixed solids and aluminum content values for sludge cake A-2, estimated product concentrations were approximately 8% as Al_2O_3, making estimated product concentrations equivalent to that of commercial-grade liquid alum.

Data in Figure 5 indicate that initial reaction temperatures following acid addition were 89° to 91°C for Runs 2-1 and 2-2. The average reaction temperature throughout the 6-hour period for Run 2-1 was 88°C (standard deviation = 1.9°C) and was well within the limits of the desired control temperature of 90°C. The desired control temperature for Run 2-2 was 50°C. After an initial elevation of temperature to 91°C, the contents of the reactor cooled over the initial 1-hour period to 53°C, at which time the temperature control system was activated. Over the remaining reaction period, the temperature was between 47 and 57°C and averaged 52°C (standard deviation = 2.7°C). Therefore, the desired control temperature was maintained for the final 5 hours of the extraction period.

Filtrate aluminum concentrations for both extractions using sludge cake A-2 are presented in Figure 6. During the initial 0.5-hour period, a major portion of the sludge

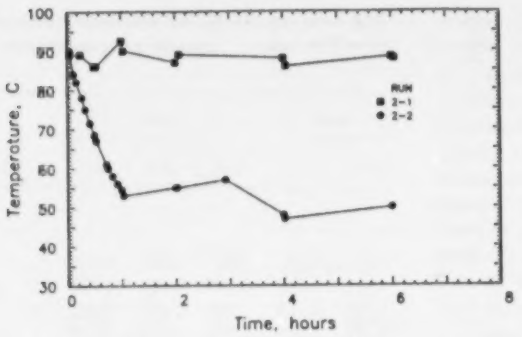

Figure 5—Temperature of reactor contents during acidic extraction of sludge cake A-2.

solids was extracted. Beyond this period, additional increases in filtrate aluminum concentrations were attributed to solubilization of residual solids and evaporational losses. Run 2-1 was conducted at 90°C and produced a filtrate aluminum concentration of 8.4% as Al_2O_3 during the first 0.5 hour, which was higher than the estimated product concentration of 7.9% as Al_2O_3. This indicated that more aluminum was contained in the sludge cake aliquot used than originally determined or the mass of dry solids added to the reactor was greater than the value calculated using wet sludge mass and solids content values. Run 2-1 ultimately produced an alum concentration of 8.8% as Al_2O_3 after 6 hours. Run 2-2 was conducted at 50°C and produced a filtrate aluminum concentration of 7.2% as Al_2O_3 during the initial 0.5-hour period. As the reaction proceeded, an aluminum concentration of 8.1% as Al_2O_3 was ultimately achieved.

Material balances for acidic extractions. Material balances on total mass and mass of aluminum were conducted on each extraction to account for the fate of various constituents (for example, sludge solids, residual aluminum, and soluble aluminum) throughout an extraction and to provide a check on analytical procedures and techniques. Results of the material balances for each extraction are included in Table 4. Overall, these data indicate good analytical and procedural balances across the experimental system, thus providing a high level of confidence associated with the results of the extractions.

With regard to total mass, it is noted that for all extractions the total mass recovered was less than 100% and ranged from 81 to 98%. For Runs 1-2 and 2-1, mass recovery was exceptionally low (that is, 81 and 84%, respectively). However, both extractions were conducted for extended reaction periods (that is, >24 hours) and were, therefore, susceptible to significant evaporational losses. The apparent evaporational losses contributed to increases in aluminum concentrations for both extractions when compared to estimated product concentrations. Specifically, Run 1-2 had a final aluminum concentration of 7.5% as Al_2O_3, an overall mass recovery of 81%, and, therefore, an apparent evaporational loss of 19% by mass. The estimated product concentration for this extraction was 5.9% as Al_2O_3 (Table 2). Thus, if the estimated product concentration was corrected for apparent water vapor loss because of evaporation, the resulting concentration would be 7.3% as Al_2O_3, which was nearly equivalent to the experimentally determined aluminum concentration of 7.5% as Al_2O_3. A similar correction was calculated for Run 2-1, resulting in a corrected value for the estimated product concentration of 9.4% as Al_2O_3, a product with a crystallization temperature of 55°C. The final sample for this extraction crystallized in the reactor, thus preventing analysis for its aluminum concentration. However, this indirectly confirmed the corrected product concentration of 9.4% as Al_2O_3 and indicated that mass loss was because of evaporational losses. The inability to conduct a filtrate aluminum analysis on this sample prevented completion of a material balance on aluminum for this extraction.

Regarding material balances on aluminum conducted for each extraction, the overall results in Table 4 indicate good closure across the respective systems. In Table 4, the aluminum output associated with residual sludge solids was calculated by assuming that residual fixed solids contained the same percentage of aluminum as the original sludge cakes. Calculated aluminum recoveries were between 99 and 104%, indicating excellent sludge aluminum recovery. However, comparing soluble aluminum output data with the original aluminum input data for each extraction indicated that the residual fixed solids may have contained much less aluminum than the original solids. This possibly accounts for the higher aluminum output values when compared to the original aluminum inputs. Moreover, residual SS data remained relatively constant with time for the extractions, indicating that the residual SS were refractory solids rather than acid-soluble, aluminum-hydroxide solids. Furthermore, this is in agreement with an earlier assumption that attributed increases in product concentrations with time to evaporation losses.

In summary, the material balance data indicate good closure on the experimental and analytical procedures for each extraction. Furthermore, the material balances for aluminum indicated that the majority of the sludge aluminum was extracted, typically in the first initial 0.5-hour period.

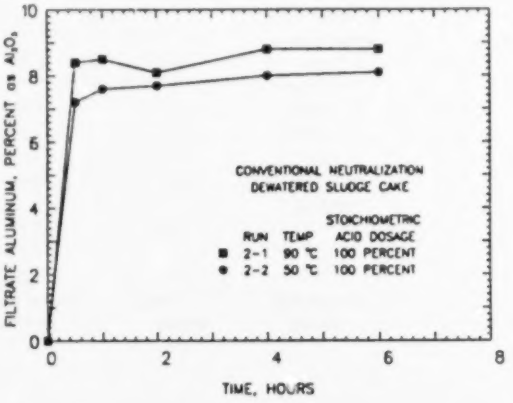

Figure 6—Filtrate aluminum concentrations during acidic extraction of sludge cake A-2.

Table 4—Material balances on total mass and aluminum for extractions of sludge cakes A-1 and A-2.

Parameter	Run 1-1	Run 1-2	Run 1-3	Run 2-1	Run 2-2
Total mass					
Input:					
Solids, g	94.4	56.8	98.7	84.9	89.4
Moisture, g	615.1	484.2	645.8	526.6	552.1
Acid, g	163.5	107.1	186.1	181.4	191.0
Total, g	873.0	648.1	930.6	792.9	832.5
Output, g	837.0	522.5	913.3	667.2	814.4
Percent recovered	96	81	98	84	98
Aluminum					
Input, g[a]	33.6	20.2	35.1	33.3	35.1
Output:					
Soluble, g	33.8	19.5	35.3	—	33.7
Residual, g[b]	1.0	1.5	1.4	—	1.0
Total, g	34.8	21.0	36.7		34.7
Percent recovered	104	104	104	N/A	99

[a] Determination based on elemental aluminum analysis of respective sludge cakes.

[b] Includes residual aluminum contained in intermittent samples; therefore, not indicative of overall extraction of aluminum from sludge cakes.

Final product quality. Analyses were conducted throughout each extraction to assess the final product quality on alum samples produced from aluminum-anodizing sludges. Specific analyses included residual SS, specific gravity, pH of a 2% dilution, congo-red test for acidity, free alum/free acid, aluminum concentration, and iron concentration. Most analyses were conducted on each individual sample taken during the respective extractions to monitor reaction kinetics; however, with the exception of aluminum concentration as presented in Figures 4 and 6, these parameters remained relatively constant throughout the respective extractions. Therefore, data for the remaining parameters are only presented for the final sample of each extraction to characterize the final product quality.

Final product quality is indicated in Table 5 for all extractions as well as typical data for a commercial-grade liquid alum. These data indicate that the quality of liquid alum produced from aluminum-anodizing sludges was generally similar to that for commercial-grade liquid alum. Two particularly important parameters are total aluminum as Al_2O_3 and residual SS concentrations. The data in Table 5 indicate that in three of the five sludge extractions, products were produced with aluminum concentrations of at least 8.0% as Al_2O_3 and were comparable in strength to commercial-grade liquid alum.

Residual SS data were not available for commercial-grade liquid alum; however, its production includes a polymer conditioning and gravity sedimentation process to remove residual solids from the final product. Residual SS measurements in Table 5 were for well-mixed samples and did not include the effects of gravity sedimentation. Visual observations, however, indicated that the majority of the SS settled quickly once mixing was terminated. Therefore, although the final product quality data indicate undesirable levels of SS in the alum products, these solids could easily be removed by gravity sedimentation. Unreacted solids ultimately could be recycled back to the batch reactor for acidic extractions, or washed to remove acidity followed by dewatering and land disposal.

Trace metal composition for the terminal sample from extraction Run 2-1, which was typical of the other runs, and two samples of commercial-grade alum products are presented in Table 6. The majority of the commercial alum is produced from bauxite and other aluminum-bearing clays and is identified as the standard grade product in Table 6. Comparing data for the alum extract from Run 2-1 and the standard grade product indicated that

Table 5—Final product quality data for liquid alum produced by acidic extractions of aluminum-anodizing sludges.

Parameter	Run 1-1	Run 1-2	Run 1-3	Run 2-1[a]	Run 2-2	Commercial-grade liquid alum[b]
Total Al_2O_3, percent	8.0	7.5	7.4	8.8	8.1	8.3
Free Al_2O_3, percent	1.2	1.0	0.5	0.1	—	0.1
Free Acid, percent	—	—	—	—	0.3	—
Total Iron, percent as Fe_2O_3	0.09	0.03	0.07	0.07	0.08	0.2 (0.005)[d]
Suspended Solids, g/L	5.6	7.1	5.9	1.9	9.1	—
Specific Gravity	1.3	1.3	1.3	1.3	1.3	1.3
pH (2% dilution)	3.8	4.0	3.7	3.4	3.0	3.5[e]
Congo Red Test, color[c]	light brown	light brown	light brown	light brown/ purple	light purple	light brown/ purple

[a] Data from sample collected after a 6-hour reaction period.

[b] Typical analyses (Reference 4).

[c] Qualitative acidity test: light brown = free alum; purple = neutral; blue = free acid.

[d] Iron-free alum.

[e] pH of 1% solution.

Table 6—Trace metal composition of alum extract from run 2-1 and commercial grade alum products.

	Concentration, mg/L		
		Commercial alum	
Metal	Alum extract (Run 2-1)	Standard grade	Iron-free grade
Ag	0.7	0.2	0.2
Cd	0.4	0.3	0.3
Cr	30	40	0.9
Ni	752	44	—
Pb	20	4	6
Sn	914	155	3
Zn	12	9	1

the concentrations of chromium, cadmium, and zinc were similar for the two products. Although the silver concentration was much higher in the alum extract, the concentration was nevertheless very low, especially when compared to the aluminum concentration.

Concentrations of nickel, lead, and tin were much higher in the alum extract, that is, by factors of approximately 17, 5, and 6, respectively, than in the standard grade product. The presence of nickel in the sludge and the alum extract was attributable to the finishing solutions used in the two-step anodizing and sealing processes, while the tin was attributed to the two-step anodizing process. While not contained at as high levels as nickel and tin, the presence of lead could be attributed to trace quantities of lead in the alloys finished and to the use of lead-lined tanks on the finishing line.

With the exception of nickel and tin, the trace metal concentration was considered to be low and in typical industrial limits. Nickel and tin levels were the highest in absolute concentrations and in the level of concentration above standard-grade products. Isolation of two-step anodizing wastes should be investigated to determine whether segregation of these wastes is necessary.

Discussion

Reclamation of the aluminum value in aluminum-anodizing sludges through commercial-strength liquid alum production using an acidic extraction is a viable alternative to conventional sludge disposal practices. With regard to the extraction process, temperature and the level of sulfuric acid addition were examined with respect to reaction kinetics and stoichiometry. The results presented in Figures 4 and 6 indicate aluminum extraction was virtually complete within 0.5 hour of acid addition. Although various operating temperatures were examined, it is noted that during the initial stages of the reaction, temperatures as high as 83° to 91°C were realized because of the heat of hydration associated with sulfuric acid addition. Therefore, the temperature effects examined were those associated with the latter stages of the extractions.

Run 2-2 was conducted at a control temperature of 50°C and a filtrate aluminum concentration of 7.2% as Al_2O_3 was produced during the initial 0.5 hours, compared to the estimated product concentration of 8.0% as Al_2O_3. As the reaction proceeded, an alum concentration of 8.1% as Al_2O_3 was ultimately achieved. The increase was primarily associated with the solubilization of residual sludge solids, because evaporational losses were low at the control temperature of 50°C. It is noted that increases in alum concentrations beyond the initial 0.5-hour period for the remaining extractions were influenced by evaporational losses and continued solubilization of residual sludge solids.

In summary, temperature is extremely critical to reaction kinetics. If temperatures are maintained above 66°C during the initial 0.5 hour of an extraction, the solubilization of sludge solids as filtrate aluminum will be virtually complete. Beyond this period, sludge solid extraction, will continue to occur at control temperatures as low as 50°C; however, the increase in resulting product concentration is minimal when compared to the initial period. It is important to note that the experimental reactor used during the extractions was susceptible to rapid heat losses associated with its high surface area to volume ratio; therefore, heat was added to the laboratory system to maintain desired temperatures. However, a full-scale batch reactor has a much lower surface area to volume ratio and is less susceptible to the rapid heat losses experienced with the laboratory-scale reactor. By maintaining the heat generated through the addition of sulfuric acid for longer times, virtually complete sludge solid extractions can be achieved without heat from external sources.

Regarding sulfuric acid additions, estimation acid requirements using a stoichiometric equation is an acceptable technique. Acid quantities are most accurately calculated based on measured aluminum content of a sludge cake. Fixed solids were shown to be a reasonably accurate measure of aluminum hydroxide content and were successfully used to calculate stoichiometric acid requirements. Site-specific data may be required to develop a correlation between fixed solids and aluminum content such that required quantities of acid could be most accurately calculated using a fixed solids analysis.

Extractions were conducted using required stoichiometric quantities of sulfuric acid ranging from 89 to 100%. Because commercial-grade alum typically contains less than 0.1% free alum as Al_2O_3,[4] the objective of an extraction is to add the required acid to extract all sludge solids and produce a final product with a free alum content of less than 0.1% without producing free acid. The extraction results indicated that acid dosages should be approximately 95% of the required stoichiometric quantity. For acid additions less than 95%, all sludge solids may not be extracted and free alum concentrations will increase beyond 0.1% as Al_2O_3. Acid additions much greater than 95% may result in a final product containing free acid. The study results also indicate that the congo-red indicator test for acidity was a quick method for determining the presence of free alum or free acid in an extraction and could be used for monitoring an extraction. Thus, additional quantities of acid or sludge solids could be added to an extraction as it proceeds to produce a final product of desirable quality.

The product-quality data for liquid alum produced by acidic extractions of aluminum-anodizing sludges were similar to typical data for commercial-grade liquid alum. Extracted alum products had product strengths greater than 8.0% as Al_2O_3 on three of five runs. The remaining runs (that is, Runs 1-2 and 1-3) resulted with products with concentrations of 7.5 and 7.4% as Al_2O_3, respectively. To produce a final product concentration equivalent to commercial-strength products (that is, 8.3% as Al_2O_3), sludge cakes with a minimum aluminum content of 5.5% aluminum (on a wet-sludge basis) are required. Using fixed solids content as a measure of aluminum hydroxide, sludge cakes require a 16% minimum fixed solids to produce alum at 8.0% as Al_2O_3. Previous research has indicated that fixed solids are typically 70 to 80% of total dry solids.[1,2] Therefore, sludge cakes of approximately 21 to 24% dry solids are required to produce an alum product at commercial-grade concentrations. Sludge cakes generated for the extractions presented herein were not dewatered to these minimum requirements; however, aluminum contents for the sludge cakes were greater than those implied when fixed solids were used as a aluminum hydroxide measure. Therefore, sufficient aluminum existed to produce final product concentrations of approximately 7.5 to greater than 8.0% as Al_2O_3.

Final or residual SS concentrations ranged from 1.9 to 9.1 g/L. Visual observations indicated that these solids settled easily and do not require polymer conditioning before sedimentation. However, these solids require removal, typically by sedimentation in alum storage tanks followed by solids removal for additional extraction with dewatered sludge cakes. An alternative method includes mechanical dewatering before land disposal. This requires washing the residual solids to remove excessive sulfuric acid and raising the pH from approximately 2 to neutral conditions.

Trace metals data presented in Table 6 for the extracted alum from Run 2-1 were similar to data for commercial-grade alum. However, concentrations of nickel, tin, and lead were much greater than typical concentrations and were attributed to finishing solutions used in the anodizing process and the use of lead-lined tanks. With the exception of nickel and tin, trace metal concentrations were considered to be low and in typical industrial limits. Segregation of finishing baths containing high levels on nickel and tin (that is, a two-step anodizing system) may be required to reduce nickel and tin concentrations.

To evaluate product quality with respect to drinking water quality, recommended maximum impurity content (RMIC) values for drinking water additives were established in a Water Chemicals Codex developed by the National Research Council.[7] Maximum contaminant levels (MCL) for drinking waters, a maximum dosage of the chemical additive, and a safety factor of 10 were used to establish RMIC values for specific impurities in a chemical additive. In the case of alum, an additional criterion was included. That was that RMIC values were applied, not to the level of an impurity in alum *per se*, but only to that level of an impurity in alum that remained in solution after coagulation (pH = 6.0), flocculation and filtration (0.45-μm pore filter) of deionized, distilled water dosed with alum [$Al_2(SO_4)_3 \cdot 14H_2O$] at 150 mg/L (that is, an Al^{+3} dose of 13.6 mg/L). Therfore, in contrast to the safety factor with a value of 10, an additional factor of unspecified value, and with an opposing effect, was included in the establishment of RMIC values for alum. This additional factor was that attributable to the removal of impurities that are co-precipitated with, complexed by, or adsorbed to aluminum hydroxide precipitates. This approach to evaluating chemical quality of a chemical additive allows for actual contaminant levels in an alum to be substantially higher than the indicated RMIC values, provided the additional contaminant is removed in the course of the coagulation, flocculation, sedimentation, and filtration processes that follow adding alum to water. Because the metal data for the alum extract and commercial alum in Table 6 do not reflect this removal following addition to water as a coagulant, it is not possible to accurately compare these data to the RMIC values. However, with this limitation stated, it is of interest to compare the impurity content of the products to the suggested RMIC values, realizing that it is possible for the impurity content to exceed the indicated RMIC value yet meet the standard when examined according to the procedures above.

RMIC values were established for alum as follows: arsenic (As), chromium (Cr), lead (Pb), and silver (Ag) are 30 mg-metal/kg-$Al_2(SO_4)_3 \cdot 14H_2O$; cadmium (Cd) and selenium (Se) are 7 mg-metal/kg-$Al_2(SO_4)_3 \cdot 14H_2O$ and mercury (Hg) is 1 mg-metal/kg-$Al_2(SO_4)_3 \cdot 14H_2O$.[7] Of these only chromium, lead, silver, and cadmium were found at signifcant levels in the alum extract and the standard-grade commercial alum (that is, that which is commonly used to treat drinking waters). In Table 7, the impurity contents and RMIC values are compared. The impurity contents for silver, cadmium, and lead were equal to or less than the RMIC values, without the benefits associated with coagulation. The impurity content for chromium for both products was above the RMIC value, with the commercial alum being highest. Therefore, in the limits of this qualified comparison, the alum extract was comparable to commercial alum and may potentially meet the Codex limits. This comparison does not, however, obviate concern for uncontrolled metals. For example, the impurity contents of nickel and tin for the alum extract

Table 7—Impurity content values for an alum extract and commercial standard-grade alum and associated RMIC values.[7]

	Impurity content		
Metal	Alum extract, mg/kg*	Standard grade commercial alum, mg/kg*	RMIC, mg/kg*
Ag	1.1	0.3	30
Cd	0.6	0.45	7
Cr	45	60	30
Pb	30	6	30

* mg of indicated metal/kg of $Al_2(SO_4)_3 \cdot 14H_2O$.

are 1129 mg/kg and 1372 mg/kg, respectively, and are well above the highest RMIC value of 30 mg/kg, further establishing the need to control or segregate these waste metals on the finishing line.

In summary, the production of liquid alum by acidic extraction of aluminum-anodizing sludges is a viable alternative to conventional sludge disposal practices. Applications could potentially include on-site reclamation and storage of alum for distribution, or transporting and combining aluminum-anodizing sludges with aluminum-bearing clays (for example, bauxite) as a feedstock for the production of commercial-grade alum. However, application practices are site-specific and the feasibility of alum reclamation must be established by evaluating anodizing systems, process wastestreams, and wastewater treatment and disposal practices.

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